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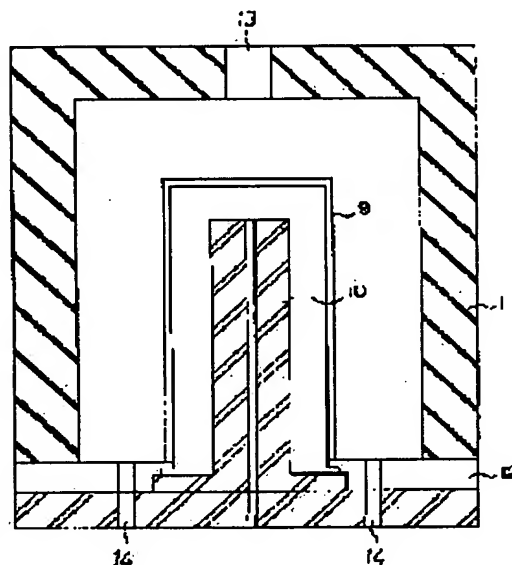
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(54) METHOD FOR FORMING SILICON OXIDE FILM OF UNIFORM FILM THICKNESS ON THREE-DIMENSIONAL CONTAINER MADE OF PLASTIC MATERIAL**(57)Abstract:**

PURPOSE: To coat a container with a transparent and uniform film superior in gas barrier properties by a method wherein an earth electrode is disposed over a film-forming surface of a container so that a distance between the surface of the container and the surface of the electrode is substantially constant and larger than a distance between a high-frequency electrode and the film-forming surface of the container, and a silicon oxide is deposited under specific conditions.

CONSTITUTION: When a film is applied to an outer surface of a container 9, a distance between a high-frequency electrode 10 and a film-forming surface of a container 9 is determined to 10mm or less, and a distance between an earth electrode 11 and the film-forming surface of the container 9 is constant and larger than the distance between the film-forming surface and the high-frequency electrode 10. A silicon oxide film is deposited with a uniform film thickness on the surface of the container 9 opposed to the earth electrode 11 under a discharge gas pressure of 0.0005-0.05-torr by introducing a plasma of a silicon oxide generated by a CVD method into between the container 9 and the earth electrode 11. In this manner, a uniform film of such an ultra-precise film thickness as to have, for example, a film thickness difference of 200Å or less is formed on the container 9 of a three-dimensional structure for remarkably improving gas barrier properties.

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CLAIMS

[Claim(s)]

[Claim 1] The distance of the front face and electrode surface which form the coat of a container in the front-face side which does not form the coat of the container of a solid configuration with which T.g. consists of a high plastics ingredient from the film production temperature of a silicon oxide thin film arranges an almost fixed RF electrode by 10mm or less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The plasma of the silicon oxide generated with the CVD method between a container and a ground electrode How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by making a silicon oxide thin film adhere to the front face which introduced and countered with the ground electrode of a container by discharge gas pressure 0.0005 - 0.05torr at the thickness of homogeneity at gas cutoff nature.

[Claim 2] The approach the distance of a container front face and a ground electrode covers with 11-100mm the silicon oxide thin film which was excellent in the container of the solid configuration which consists of an almost fixed plastics ingredient indicated by claim 1 at gas cutoff nature.

[Claim 3] How to cover the silicon oxide thin film which was excellent in the container of a solid configuration with which a ground electrode consists of a plastics ingredient which are a container covering surface and one electrode which has the opposite front face of the same configuration mostly, and which was indicated by claims 1 or 2 at gas cutoff nature.

[Claim 4] How to cover the silicon oxide thin film which was excellent in the container of a solid configuration with which an RF electrode consists of a plastics ingredient indicated by claim 1 thru/or any 1 term of 3 which is the covering surface of a container, and one electrode which has the inside of the same configuration mostly at gas cutoff nature.

[Claim 5] The approach the silicon oxide thin film formed in the front face of the container of the solid configuration which consists of a plastics ingredient covers [thickness] with refractive indexes 1.4-1.5 the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient indicated by claim 1 thru/or any 1 term of 4 which is 300-2000A at gas cutoff nature.

[Claim 6] The distance of the front face and electrode surface which form covering of a container in the front-face side which does not form the coat of the container of a solid configuration with which T.g. consists of a high plastics ingredient from the film production temperature of a silicon oxide thin film arranges an almost fixed RF electrode by 10mm or less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The organic silicon compound which consists of silicon, oxygen, and carbon at least by the low-temperature plasma method The plasma and nothing, Introduce this plasma between a container and a ground electrode, carry out a polymerization by discharge-gas-pressure 3×10^{-3} - 3×10^{-2} torr, and a silicon compound polymer thin film is formed in a container inside. With subsequently, a CVD method How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by supplying the plasma of the generated silicon oxide and forming the coat of a silicon oxide on a silicon compound thin film by discharge gas pressure 0.0005 - 0.05torr at gas cutoff nature.

[Claim 7] The approach a silicon compound coat covers [thickness / those with 0.005 micrometers - 0.05 micrometer, and a silicon oxide coat] with refractive indexes 2.0-2.3 the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient whose thickness is 300-2000A, and which was indicated by claim 6 at gas cutoff nature with refractive indexes 1.4-1.5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of covering the thin film of the transparent silicon compound which was excellent in the container which consists of a plastics ingredient used for a package at gas cutoff nature.

[0002]

[Description of the Prior Art] A packing material needs to prevent transparency of gas for protection of contents, and preservation, and the attempt of the conventional versatility is made. For example, prepare inorganic enveloping layers, such as silicon oxide and aluminum oxide, the laminating of the gas cutoff nature resin layers, such as a polyvinylidene chloride, is carried out, or to carry out the laminating of the metal film of aluminum foil has been tried. In addition, the laminated film which covered the synthetic resin same on a plastics film as the plastics with the shape of a thin film by vacuum deposition and sputtering to JP,3-183759,A, formed the organic layer, vapor-deposited the inorganic substance, formed the mixolimnion of the organic substance and an inorganic substance on it, and formed the inorganic layer on it further is shown. In order for the inorganic substance of an enveloping layer to be completely different matter, for these plastics to cover the same synthetic resin as plastics in the shape of a thin film since compatibility is scarce, and to improve fixable [of inorganic covering], the blend layer of synthetic resin and an inorganic substance is formed in the middle, but since, as for the front face of a blend layer, not the field of only an inorganic substance but the field of synthetic resin exists, fixable [of an inorganic layer] does not improve to the expected degree. Moreover, it is inapplicable to the Plastic solid except a sheet-like object to vapor-deposit synthetic resin and an inorganic substance at two processes. Furthermore, since molecular weight will fall if synthetic resin is vapor-deposited, as for the container which consists of this plastics ingredient, workability deteriorates. this invention person applied for JP,5-345383,A invention and Japanese-Patent-Application-No. No. 224903 [five to] invention previously. Invention of this etc. is epoch-making invention from which the conventional packing material completely differs, and the fault of the conventional packing material was solved. However, although the coat of the thickness of homogeneity could be formed about the container which has three-dimensional structure, there was a little inadequate point in forming the coat of the thickness of ultraprecise homogeneity. And ultraprecise thickness is required of the package of a special application, for example, a special chemical etc.

[0003]

[Problem(s) to be Solved by the Invention] In the container of three-dimensional structure, the difference of thickness forms the coat of ultraprecise thickness 200A or less, and this invention solves the problem of the above-mentioned thickness nonuniformity, and carries out improvement in ***** of the gas cutoff nature.

[0004]

[The means which solved the technical problem] "This invention, the distance of the front face and electrode surface which form covering of a container in the front-face side which does not form the coat of the container of a solid configuration with which T.g. consists of a high plastics ingredient from the film production temperature of a 1. Silicon oxide thin film arranges an almost fixed RF electrode by 10mm or less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The plasma of the silicon oxide generated with the CVD method between a container and a ground electrode How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by making a silicon oxide thin film adhere to the front face which introduced and countered with the ground electrode of a container by discharge gas pressure 0.0005 - 0.05torr at the thickness of homogeneity at gas cutoff nature.

2. Approach distance of container front face and ground electrode covers with 11-100mm silicon oxide thin film which was excellent in container of solid configuration which consists of plastics ingredient indicated by the 1st almost fixed term at gas cutoff nature.
3. How to cover silicon oxide thin film which was excellent in container of solid configuration with which ground electrode consists of plastics ingredient indicated by container covering surface, the 1st term which is one electrode which has opposite front face of the same configuration mostly, or the 2nd term at gas cutoff nature.
4. How to cover silicon oxide thin film which was excellent in container of solid configuration with which RF electrode consists of plastics ingredient indicated by any 1 term of covering surface of container, the 1st term which is one electrode which has inside of the same configuration mostly, or the 3rd term at gas cutoff nature.
5. Approach silicon oxide thin film formed in front face of container of solid configuration which consists of plastics ingredient covers [thickness] with refractive indexes 1.4-1.5 silicon oxide thin film which was excellent in container of solid configuration which consists of plastics ingredient indicated by any 1 term of the 1st term which is 300-2000A thru/or the 4th term at gas cutoff nature.
6. Distance of Front Face and Electrode Surface Which Form Covering of Container in Front-Face Side Which Does Not Form Coat of Container of Solid Configuration with which T.G. Consists of a High Plastics Ingredient from Film Production Temperature of Silicon Oxide Thin Film Arranges Almost Fixed RF Electrode by 10Mm or Less. A ground electrode with a distance of the front face of a container and an electrode surface large almost more fixed than the distance on an RF electrode and the front face of a container which forms a coat is installed in the front-face side which forms a coat. The organic silicon compound which consists of silicon, oxygen, and carbon at least by the low-temperature plasma method The plasma and nothing, Introduce this plasma between a container and a ground electrode, carry out a polymerization by discharge-gas-pressure 3×10^{-3} - 3×10^{-2} torr, and a silicon compound polymer thin film is formed in a container inside. With subsequently, a CVD method How to cover the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient characterized by supplying the plasma of the generated silicon oxide and forming the coat of a silicon oxide on a silicon compound thin film by discharge gas pressure 0.0005 - 0.05torr at gas cutoff nature.

7. approach a silicon compound coat covers [thickness / those with 0.005 micrometers - 0.05 micrometer, and a silicon oxide coat] with refractive indexes 2.0-2.3 the silicon oxide thin film which was excellent in the container of the solid configuration which consists of a plastics ingredient whose thickness is 300-2000Å, and which was indicated by the 6th term at gas cutoff nature with refractive indexes 1.4-1.5. " -- it is related.

[0005]

[Function] the 1st description which does a special operation of this invention so is having arranged the external electrode which surrounded the container to the exterior of the container of a solid configuration, and the distance of the external surface of a container and an external electrode surface being about 1 law, and having arranged inside a container the internal electrode whose distance of the inside of a container and an electrode surface is about 1 law. Furthermore, it is the description that the distance of the front face of an external electrode and a container inside is 10mm or less when covering a thin film to the inside of a container, and the distance of the front face of an internal electrode and container external surface is 10mm or less when covering a thin film on the external surface of a container. The distance on an electrode and the front face of a container is kept constant for setting field strength distribution constant. The distance of an RF electrode and the front face in which covering of a container is prepared must be 10mm or less. It is because the problem to which the gas cutoff nature of a coat falls rapidly when it comes to 10mm or more arises. Moreover, the distance on a ground electrode and the front face of covering of a container must be larger than the distance of the field and RF electrode which prepare covering. The discharge stabilized when the front face in which covering of a container is prepared, the distance of an RF electrode, and the distance of the front face in which covering of a container is prepared, and a ground electrode were equal is not obtained. And on the discharge conditions of this invention, discharge discharges in the one where the distance on an electrode and the front face of a container is larger. So, in this invention, enlarge distance of a container front face and a ground electrode, it is made to discharge between them, and a coat is formed. The distance on a ground electrode and the front face of a container is 11-100mm preferably, and is 11-70mm preferably.

[0006] The 2nd description of this invention is using one ground electrode and one RF electrode. The thickness of the coat which becomes fixed [the intensity distribution of electric field] to a precision, and is formed serves as homogeneity by using such two electrodes together.

[0007] The plasma of a silicon oxide is made to generate using a CVD method, by 0.0005 or less torrs, a film production rate falls [discharge gas pressure] extremely, the 3rd description of this invention is in the condition which cannot carry out real film production, and the problem to which the gas cutoff nature of a coat falls [gas pressure] rapidly by 0.05 or more torrs produces it.

[0008] The 4th description of this invention is using the container which T.g.'s formed with the high plastics ingredient from the film production temperature of silicon oxide thin ** as a container which covers. It is because deformation of a container must be avoided at the time of film production in order to form an ultraprecise thin film. Such 1st description - the 4th description are put together, and the plasma of a silicon oxide is introduced between an electrode surface and a container wall. Since field strength distribution in the meantime is fixed, plasma concentration becomes fixed, and on a container wall, a silicon oxide deposits and is covered with uniform thickness. In this way, the silicon oxide coat of fixed thickness is formed.

[0009] The number of internal electrode and external electrodes must also be one, respectively, and using two or more electrodes must avoid. If two or more electrodes are used, a uniform coat cannot be formed even if it uses a CVD method. this invention person studied [why a uniform coat is not formed and] many things. For example, as shown in drawing 3, two or more electrodes have been arranged so that distance with the external surface of a container may become fixed, and when the silicon oxide was covered with the CVD method, the thickness of a coat did not become fixed as the next example of a comparison showed. Although thickness became homogeneity when it covered rotating a container at a fixed rate furthermore, the gas cutoff nature of the covered film did not improve. Since the field strength distribution which each electrode has since two or more electrodes were used interferes mutually, it influences, the concentration of the plasma changes and this invention person is the mixture of the film formed of different field strength when thickness did not become homogeneity and a container was rotated, he thinks that the film excellent in gas cutoff nature is not formed.

[0010] Although this invention uses a CVD method, the CVD method using a RF, an alternating current, and a direct current etc. is used. A refractive index is [the thickness of the silicon oxide coat formed of this invention] 300-2000Å in 1.4-1.5. By 300Å or less, the continuation film is not obtained for thickness, gas cutoff nature does not improve, and even if it covers 2000Å or more, improvement in gas cutoff nature is seldom found, but the problem which the film destroys with internal stress conversely arises. As for the ingredient used in order to form the silicon oxide plasma with a CVD method by this invention, helium, Ar gas, etc. are used as organosilicon compounds, such as SiH₄, NO_x gas, oxygen gas, TEOS (tetra-ethoxy silane), and HMDSO (hexa methyl disiloxane), NO_x, oxygen gas, and plasma auxiliary gas. Thus, the formed silicon oxide coat is the container which did the outstanding gas screening effect so and was very excellent in the usual application.

[0011] The 5th description of this invention can be covered to both of the fields by choosing whether a ground electrode is arranged to the inside side of a container, or it arranges to an external surface side. Moreover, inside-and-outside both sides can also be covered by changing the location of a ground electrode and carrying out two or more times.

[0012] The silicon compounds used for forming a silicon oxide coat by this invention are liquefied monomers, such as a silane, and a vinyl ethoxy silane, phenyltrimethoxysilane.

[0013] This invention to the side which does not form the coat of the container of the solid configuration which consists of a plastics ingredient with T.g. higher than the film production temperature of a silicon oxide thin film again The distance of the front face and electrode surface in which covering of a container is prepared installs an almost fixed RF electrode by 10mm or less. Moreover, to the side which forms the coat of a container, the distance of a container front face and an electrode surface arranges an RF electrode and a ground electrode large almost more fixed than the distance on the front face of a container. The organic silicon compound which consists of silicon, oxygen, and carbon at least by the low-temperature plasma method The plasma and nothing, Supply this plasma between a container front face and a ground electrode, carry out a polymerization by gas pressure 3x10⁻³ - 3x10⁻²torr, and a silicon compound polymer thin film is formed in a container inside. With subsequently, a CVD method The approach of forming the silicon oxide coat of the thickness of homogeneity in the container which consists of a plastics ingredient characterized by supplying the plasma of the generated silicon oxide and discharge forming the coat of a silicon oxide on a silicon compound thin film by gas pressure 0.0005 - 0.05torr is also included. While the coat which consists of this bilayer is excellent in gas cutoff nature, the amount of steam transparency does so the very high steam screening effect not more than 0.1 g/m²day. If a ground electrode and an RF electrode are arranged and this silicon compound polymer coat and a silicon oxide coat are formed, since a uniform coat is formed, gas cutoff nature of both coats will improve remarkably.

[0014] Although that academic elucidation is not necessarily enough in why such special effectiveness will be done so if the laminating of two sorts of these layers is carried out in this sequence, this invention does so the operation effectiveness which carries out repetitive reappearance. this invention person thinks that ***** is large with the gas screening effect of a silicon oxide layer

being based on the stable fixable one of the silicon oxide particle supplied on a covering base. That is, the supplied particle moves in a plastics base top, is stabilized and is established in the most stable location. In this case, if the polymer coat of the silicon compound containing silicon, carbon, and oxygen is formed on the plastics base, a silicon oxide particle will be stabilized good and will be established. And I think that it is because the distribution becomes uniform, a silicon oxide particle is piled up further and silicon oxide covering is formed on the stable silicon oxide particle, so it becomes close covering.

[0015] Moreover, I think that it is because it will become few close coats of the defect in which fixable is more high, about the super-steam gas cutoff nature not more than 0.1 g/m²day being shown if the silicon compound polymer coat of the first pass and the silicon oxide coat of the second layer are within the limits of a specific refractive index, respectively.

[0016] In the presentation of the silicon in the first pass, carbon, and oxygen, 15% or more of silicon, 20% or more of carbon, and the remainder contain oxygen, and the 1st organosilicon compound polymer enveloping layer is a 0.005 micrometers - 0.05 micrometers film. If the thickness of an enveloping layer becomes thicker than this, gas cutoff nature will worsen.

[0017] Special organosilicon compound polymer covering of such the first pass can plasma-ize organosilicon compound monomers, such as for example, hexa methyl disiloxane, and can form them by carrying out a polymerization on a plastics base. The refractive index of the coat formed by adjusting the gas pressure at the time of this polymerization to 3×10^{-3} to 3×10^{-2} torr can be set to 2.0-2.3. Conventionally, although it is other applications, since discharge gas pressure is the range of 0. number torr to number +torr, the plasma-CVD method learned is understood that the plasma-CVD method used by this invention is special.

[0018] As an organic silicon compound monomer used by this invention, they are vinyltriethoxysilane, vinyltrimetoxysilane, a tetramethoxy silane, a tetra-ethoxy silane, phenyltrimethoxysilane, octamethylcyclotetrasiloxane, methyl trimetoxysilane, methyl triethoxysilane, 1133-tetramethyl disiloxane, hexane methyl disiloxane, etc. Compounds, such as this, are used also for formation of a **** oxide coat.

[0019]

[Example] An example is given and it is explained that this invention is intelligible.

[0020] Example 1 drawing 1 is an RF plasma CVD system which forms the organic silicon compound coat used by this invention. This equipment consists of fixture 8 grade for samples installed between the cylindrical ground electrodes 2 and two electrodes with the bell jar mold vacuum chamber 1 made from stainless steel with an equipped with the inlet 6 and the oxygen gas inlet 7 which introduce a silane and an ordinary temperature liquid monomer by the gaseous state diameter of 60cm, the JEOL Co., Ltd. make and RF generator 5, a matching box [4] and disc-like RF electrode 3 with a diameter of 13cm, a diameter [of 20cm, and a height of 1.5cm. The equipment of this drawing 1 can perform both organosilicon compound covering and covering of the silicon oxide film which is a gas filter layer. a vacuum pump should use an oil sealed rotary pump and an oil diffusion pump, and should always continue a pump during pretreatment and membrane formation -- pretreatment and a thin film covering trial were performed. As an ordinary temperature liquid monomer, oxygen gas was used as hexa methyl disiloxane (it is described as Following HMDSO), and reactant gas. It is introduced in a chamber by another root, and is mixed within a ground electrode, and these gas is emitted in a chamber, respectively. The ground electrode and the RF electrode have been arranged to parallel (distance of 70mm), and installed the 100micro polycarbonate (it is described as Following PC) sheet in the RF electrode and the ground electrode (it is 5mm from an RF electrode) with the insulating sample fixture as a sample. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, oxygen gas was introduced and it continued until the degree of vacuum in a chamber was set to 1×10^{-3} torr, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 2×10^{-3} torr. From the RF generator, incidence power 200W were introduced in the chamber via the matching box, the mixed plasma of oxygen and HMDSO was generated, it held for 10 minutes, and oxidation silicon **** was formed on PC sample. The amount of steam transparency of this layered product was measured with the amount measuring instrument of steam transparency made from Mocon, and was shown in Table 1.

[0021] Except having installed the location of the sample installed in example 2 and example of comparison 1 RF electrode, and ground inter-electrode in 3, 7, 9, 23, and 40mm on the RF substrate, it was the same conditions as an example 1, and oxidation silicon **** was formed on PC sample, the amount of steam transparency was measured, and it was shown in Table 1 with the example 1.

[0022]

[Table 1]

| | 高周波電極-基板 間距離 (mm) | 水蒸気透過量 g/m ² day |
|-------|----------------------|--------------------------------|
| 実施例 1 | 5 | 0.07 |
| 実施例 2 | 0 | 0.10 |
| | 3 | 0.09 |
| | 7 | 0.07 |
| | 9 | 0.10 |
| 比較例 1 | 23 | 1.3 |
| | 40 | 3.1 |

[0023] Except that thickness used the -15 to 105 degrees C sheet plastic for example 3 and example of comparison 2 sample by 100micro-280micro, glass transition temperature (it is described as Following Tg) is an example 1 and the same conditions, oxidation silicon **** was formed on the sample, the amount of steam transparency was measured, and it was shown in Table 2. As a result of measuring the temperature on the front face of a sample with an optical-fiber type thermometer, on this condition, it was 45 degrees C.

[0024]

[Table 2]

| | | |
|--|--|--|
| | | |
|--|--|--|

| | 基板のTg (°C) | 水蒸気透過量 |
|-------|------------|--------|
| 実施例 3 | 125 | 0.03 |
| | 115 | 0.04 |
| | 105 | 0.03 |
| | 97 | 0.04 |
| | 91 | 0.08 |
| | 87 | 0.1 |
| 比較例 2 | -10 | 0.4 |

[0025] Example 4 drawing 2 is the explanatory view showing the cross section of the electrode for container external surface covering used for this invention. Nine in drawing is a closed-end cylindrical shape [made from polyethylene terephthalate (henceforth, PET)]-like container. 10 is an internal RF electrode and the outside surface serves as the same configuration as the external surface of a closed-end cylindrical shape-like container. And the distance of the outside surface of an electrode 10 and a container outside surface is fixed at about 5mm. 11 is an external ground electrode, the inside of an electrode 11 is the almost same configuration as the external surface of the closed-end cylindrical cup 9, and both distance is almost fixed at about 12mm. The ground electrode 11 and RF electrode 10 are arranged through the insulator 12, a gas inlet 13 is installed in the upper part of the ground electrode 11, and the flueing opening 14 is installed in the lower part of the electrode for container external surface covering again. From a gas inlet 13, reactant gas and monomer gas are introduced in an electrode, are plasma-ized, flow along the external surface of the closed-end cylindrical shape-like container 9, and are exhausted out of an electrode from the flueing opening 14. A silicon oxide coat is formed in the outside surface of the closed-end cylindrical shape-like container 9 in this electrode. With the electrode for container external surface covering which has arranged the closed-end cylindrical shape-like container 9, the equipment shown in drawing 1 was used and the silicon oxide coat was formed in the container outside surface. Formation of an oxidation silicon object coat removed the fixture 8 for samples in drawing 1, has arranged the electrode for container external surface covering of drawing 2 between the RF electrode 3 ground electrodes 2 in drawing 1, and connected the ground electrode 11 of the cylindrical ground electrode 2 and the electrode for container external surface covering, and connected disc-like RF electrode 3 and RF electrode 10 for container external surface covering. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, oxygen gas was introduced and it continued until the degree of vacuum in a chamber was set to 1×10^{-3} torr, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 2×10^{-3} torr. From the RF generator, incidence power 200W were introduced in the chamber via the matching box, the mixed plasma of oxygen and HMDSO was generated, it held for 10 minutes, and oxidation silicon **** was formed in the external surface of a closed-end cylindrical shape-like container. Oxidation silicon object thickness distribution of the drum section of a closed-end cylindrical shape-like container and the amount of steam transparency were measured, and it was shown in Table 3.

[0026] As shown in example of comparison 3 drawing 3, it covered as the same conditions as an example 4 from cylindrical shape-like container external surface at the equal distance except having arranged four external RF electrodes 15 at the location which serves as equiangular [of 90 degrees] from a cylinder core on the outside of the same closed-end cylindrical shape-like container 9 as an example 4. Oxidation silicon object thickness distribution of the drum section of the closed-end cylindrical shape-like container 9 and the amount of steam transparency were measured, and it was shown in Table 3 with the example 4. Drawing 4 is the explanatory view which saw the covering equipment of drawing 3 from the upper part, and measuring points 0D, 45D, and 90D are specified.

[0027] It covered as the same conditions as the example 3 of a comparison except carrying out axial rotation of the example of comparison 4 closed-end cylindrical shape-like container 1 by 4rpm. Oxidation silicon object thickness distribution of the drum section of the closed-end cylindrical shape-like container and the amount of steam transparency were measured, and it was shown in Table 3 with the example 4 and the example 3 of a comparison.

[0028]

[Table 3]

| 測定位置 | 膜厚 (Å) | | | 屈折率 | | | 水蒸気透過量 g/m ² day |
|-------|--------|------|-----|------|------|------|--------------------------------|
| | 0D | 45D | 90D | 0D | 45D | 90D | |
| 実施例 4 | 950 | 980 | 930 | 1.45 | 1.47 | 1.44 | 0.02 |
| 比較例 3 | 510 | 1680 | 620 | 1.42 | 1.69 | 1.44 | 1.85 |
| 比較例 4 | 940 | 990 | 950 | 1.55 | 1.60 | 1.56 | 1.05 |

[0029] Example 5 drawing 5 is the explanatory view showing the cross section of the electrode for container inside covering used for this invention. Nine in drawing is a cup configuration container made from an annular olefin copolymer (henceforth, COC). 15 is an external RF electrode and the internal surface serves as the same configuration as the inside of a cup configuration container. And the distance of the internal surface of an electrode 15 and a container internal surface is fixed at about 5mm. 16 is an internal ground electrode, the external surface of an electrode 16 is the almost same configuration as the inside of the cup configuration container 9, and both distance is almost fixed at about 20mm. The ground electrode 16 and RF electrode 15 are arranged through the insulator 12, a gas inlet 13 is installed in the lower part of the ground electrode 16, and the flueing opening 14 is installed in the upper part of a ground electrode again. From a gas inlet 13, reactant gas and monomer gas are introduced in an electrode, are plasma-ized, flow in accordance with the inside of the cup configuration container 1, and are exhausted out of an electrode from the flueing opening 14. A silicon oxide coat is formed in the internal surface of the cup configuration container 9 in this electrode. With the electrode for container inside covering which has arranged the cup configuration electrode, the equipment shown in drawing 1 was used and the silicon oxide coat was formed in the container internal surface. Formation of an oxidation silicon object coat removes the fixture 8 for samples in drawing, and arranges the electrode for container inside covering of drawing 5 between RF electrode 3 in drawing 1, and the ground electrode 2. Connect the ground electrode 16 of the cylindrical ground electrode 2 and the electrode for container inside covering, and connect disc-like RF electrode 3 and RF electrode 15 for container inside covering, introduce SiH₄ gas from a monomer

inlet, and oxygen is introduced from an oxygen gas inlet. These mixed-gas plasma was formed, by 3×10^{-3} torr, the oxidation silicon film was deposited in the inside of a cup ** -like container, and the discharge pressure was carried out to it. As a result of measuring the amount of steam transparency of the cup top container which covered the oxidation silicon film, it was 0.02 g/m²day (40-degree-C90%RH).

[0030] The closed-end cylindrical shape [made from example 6 polyethylenenaphthalate (it is described as Following PEN)] -like container was used, with the electrode for container external surface covering, the equipment shown in drawing 2 was used and the HMDSO polymer coat and the silicon oxide coat were formed in the container outside surface. The coat approach covered as the same conditions as an example 4 except the conditions described as a closed-end cylindrical shape-like container below. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 3×10^{-3} torr - 10×10^{-3} torr. From the RF generator, incidence power 400W were introduced into the chamber, the plasma of HMDSO was generated, it held for 1 minute, and the HMDSO polymer coat was formed in the external surface of a closed-end cylindrical shape-like container. Then, the degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr with the oil sealed rotary pump and the oil diffusion pump, and the coat of a silicon oxide was formed on the HMDSO polymerization film like the example 5. It was an ellipsometer about the refractive index of the film of the closed-end cylindrical shape-like container which covered these coats, and thickness, and with the weight method, the amount of steam transparency was measured and it was shown in Table 4.

[0031]

[Table 4]

| | H M D S O | | HMDSO膜 | | 二層膜の |
|-------|-----------|-------|--------|-----|--------|
| | 濃 度 | 被覆時間 | 屈折率 | 膜厚 | 水蒸気透過量 |
| 実施例 6 | 3 | 0.5 分 | 2.05 | 60 | 0.04 |
| | 3 | 1.0 分 | 2.05 | 100 | 0.03 |
| | 3 | 2.0 分 | 2.05 | 210 | 0.05 |
| | 8 | 0.5 分 | 2.25 | 80 | 0.02 |
| | 8 | 1.0 分 | 2.25 | 150 | 0.02 |
| | 8 | 2.0 分 | 2.25 | 320 | 0.03 |
| | 10 | 0.5 分 | 2.04 | 120 | 0.05 |
| | 10 | 1.0 分 | 2.04 | 240 | 0.08 |
| | 10 | 2.0 分 | 2.04 | 480 | 0.08 |

[0032] (**) unit [of HMDSO concentration]; -- unit;g/m² of 1×10^{-3} torr, the unit; angstrom of thickness, and the amount of steam transparency -- day and at 40-degree-C90%RH and [0033] Except the concentration of example of comparison 5HMDSO being [the covering time amount of 1.5×10^{-3} torr, 20×10^{-3} torr, and the HMDSO film] 0.2 and 5 minutes, the refractive index and thickness of the HMDSO film which were covered on the external surface of the same closed-end cylindrical shape-like PEN container as an example 6 were measured by the ellipsometer, and the amount of steam transparency of the HMDSO film and a silicon oxidation cascade screen was measured with the weight method, and it was made Table 5.

[0034]

[Table 5]

| | H M D S O | | HMDSO膜 | | 二層膜の |
|-------|-----------|-------|--------|------|--------|
| | 濃 度 | 被覆時間 | 屈折率 | 膜厚 | 水蒸気透過量 |
| 比較例 5 | 2 | 0.2 分 | 1.76 | 30 | 0.15 |
| | 2 | 5 分 | 1.78 | 770 | 0.45 |
| | 20 | 0.5 分 | 1.68 | 300 | 0.32 |
| | 20 | 5 分 | 1.66 | 6000 | 0.47 |
| 未被覆 | | | | | 0.49 |

[0035] (**) unit [of the concentration of HMDSO]; -- unit;g/m² of the amount of steam transparency of the thickness; angstrom of 1×10^{-3} torr and the HMDSO film, and the bilayer film -- day and at 40-degree-C90%RH and [0036] The closed-end cylindrical shape [made from example 7 polyethylenenaphthalate (it is described as Following PEN)] -like container was used, with the electrode for container external surface covering, the equipment shown in drawing 2 was used and the HMDSO polymer coat and the silicon oxide coat were formed in the container outside surface. The coat approach covered as the same conditions as an example 4 except the conditions described as a closed-end cylindrical shape-like container below. The degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr (ionization vacuum gage) with the oil sealed rotary pump and the oil diffusion pump, and the HMDSO steam was introduced until the degree of vacuum in a chamber was set to 4×10^{-3} torr. From the RF generator, incidence power 400W were introduced in the chamber, the plasma of HMDSO was generated, it held for 1 minute, and the HMDSO polymer coat was formed in the external surface of a closed-end cylindrical shape-like container. Then, the degree of vacuum in a chamber was lengthened to the vacuum to $2 - 3 \times 10^{-5}$ torr with the oil sealed rotary pump and the oil diffusion pump, it is the range of 0.5-2.5 about the ratio of concentration (the ratio of the degree of vacuum in a chamber by the ionization vacuum gage; HMDSO/oxygen) of a HMDSO steam and oxygen, and the coat of a silicon oxide was formed for the covering time amount of the oxidation silicon film on the HMDSO polymerization film like the example 5 except 5 - 20 minutes. It was an ellipsometer about the refractive index of the film of the closed-end cylindrical shape-like container which covered these coats, and thickness, and with the weight method, the amount of steam transparency was measured and it was shown in Table 6.

[0037]

[Table 6]

| | HMDSO/O ₂ の比率 | 酸化珪素膜 の被覆時間 | 酸化珪素膜 | | 二層膜の 水蒸気透過量 |
|-------|-----------------------------|----------------|-------|------|----------------|
| | | | 屈折率 | 膜厚 | |
| 実施例 7 | 0.5 | 5.0 | 1.43 | 510 | 0.03 |
| | 0.5 | 10.0 | 1.44 | 1060 | 0.02 |
| | 0.5 | 20.0 | 1.44 | 1980 | 0.02 |
| | 1.0 | 5.0 | 1.45 | 490 | 0.02 |
| | 1.0 | 10.0 | 1.45 | 1080 | 0.02 |
| | 1.0 | 20.0 | 1.46 | 2010 | 0.02 |
| | 2.5 | 5.0 | 1.46 | 520 | 0.03 |
| | 2.5 | 10.0 | 1.46 | 1050 | 0.04 |
| | 2.5 | 20.0 | 1.46 | 2030 | 0.05 |

[0038] (**) unit;g/m2 of the amount of steam transparency of the unit; angstrom of the thickness of a part for unit [of the covering time amount of the oxidation silicon film];, and the oxidation silicon film, and the bilayer film -- day and at 40-degree-C90%RH and [0039] It is 0.5 and 5 about the ratio of concentration (the ratio of the degree of vacuum in a chamber by the ionization vacuum gage; HMDSO/oxygen) of an example of comparison 6HMDSO steam, and oxygen, and the coat of a silicon oxide was formed for the covering time amount of the oxidation silicon film on the HMDSO polymerization film like the example 7 except 2 minutes and 25 minutes. It was an ellipsometer about the refractive index of the film of the closed-end cylindrical shape-like container which covered these coats, and thickness, and with the weight method, the amount of steam transparency was measured and it was shown in Table 7.

[0040]

[Table 7]

| | HMDSO/O ₂ の比率 | 酸化珪素膜 の被覆時間 | 酸化珪素膜 | | 二層膜の 水蒸気透過量 |
|-------|-----------------------------|----------------|-------|------|----------------|
| | | | 屈折率 | 膜厚 | |
| 比較例 6 | 0.2 | 2 分 | 1.38 | 180 | 0.46 |
| | 0.2 | 25 分 | 1.39 | 2350 | 0.14 |
| | 5.0 | 2 分 | 1.59 | 190 | 0.48 |
| | 5.0 | 25 分 | 1.60 | 2530 | 0.25 |
| 未被覆 | | | | | 0.49 |

[0041] (**) unit [of the thickness of the oxidation silicon film]; -- unit;9 of the amount of steam transparency of angstrom and the bilayer film/m2 -- day and at 40-degree-C90%RH and [0042]

[Effect of the Invention] Since this invention forms the silicon oxide thin film of the refractive index of the fixed range in the plastics container of a solid configuration by the thickness of homogeneity, the container which was excellent in gas barrier nature can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view of the high frequency BURAZUMA CVD system used by this invention.

[Drawing 2] It is the explanatory view of the container external surface covering equipment used by this invention.

[Drawing 3] It is the explanatory view of the example of a comparison.

[Drawing 4] It is the explanatory view showing the measuring point of the equipment of drawing 3.

[Drawing 5] It is the explanatory view of the equipment for container inside covering used by this invention.

[Description of Notations]

- 1 Vacuum Chamber
- 2 Ground Electrode
- 3 RF Electrode
- 4 Match Box
- 5 High Periphery Power Source
- 6 Gas Inlet
- 7 Gas Inlet
- 8 Fixture for Vacuum Chamber Samples
- 9 Cylindrical Cup
- 10 Internal RF Electrode
- 11 External Ground Electrode
- 12 Insulator
- 13 Gas Inlet
- 14 Gas Exhaust
- 15 External RF Electrode
- 16 Internal Ground Electrode

[Translation done.]

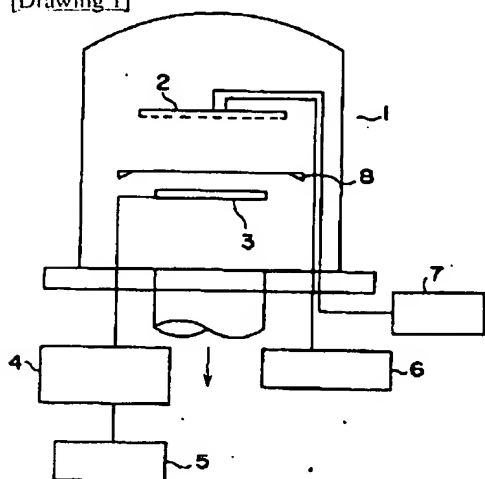
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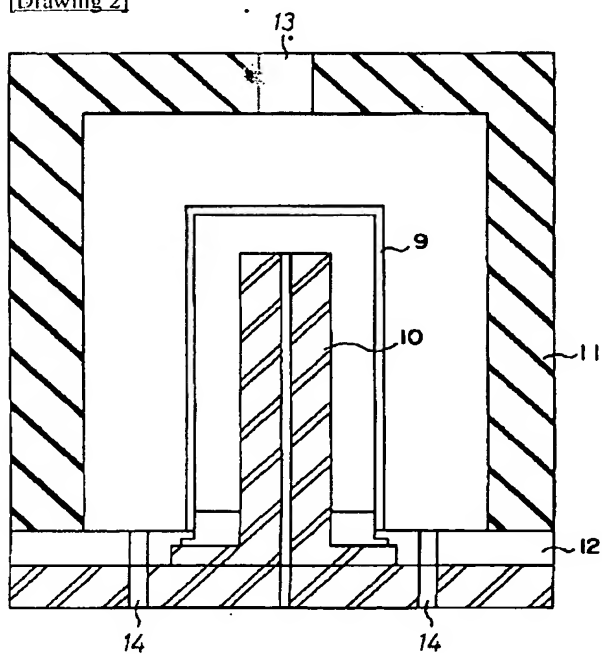
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DRAWINGS

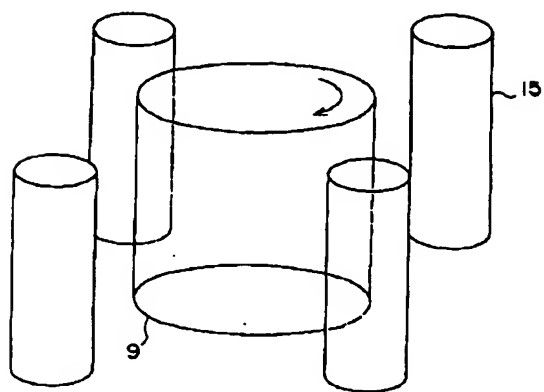
[Drawing 1]



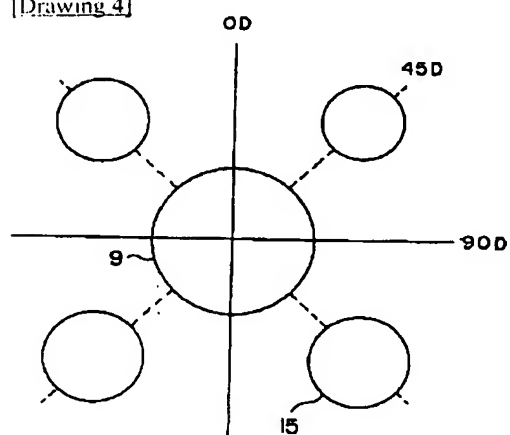
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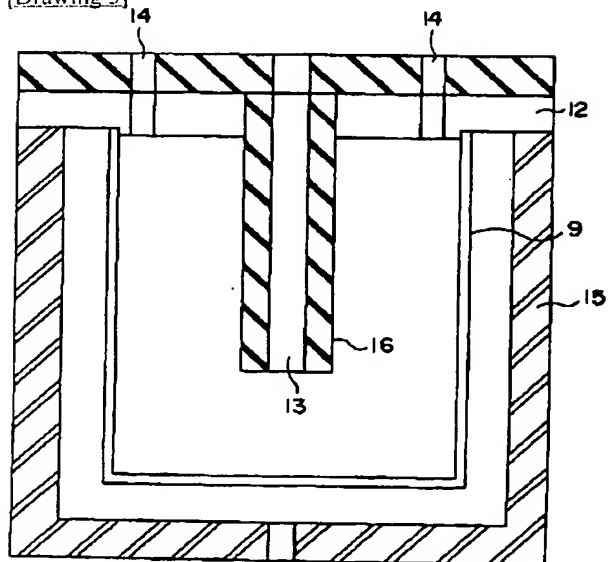
[Drawing 3]



[Drawing 4]



[Drawing 5]



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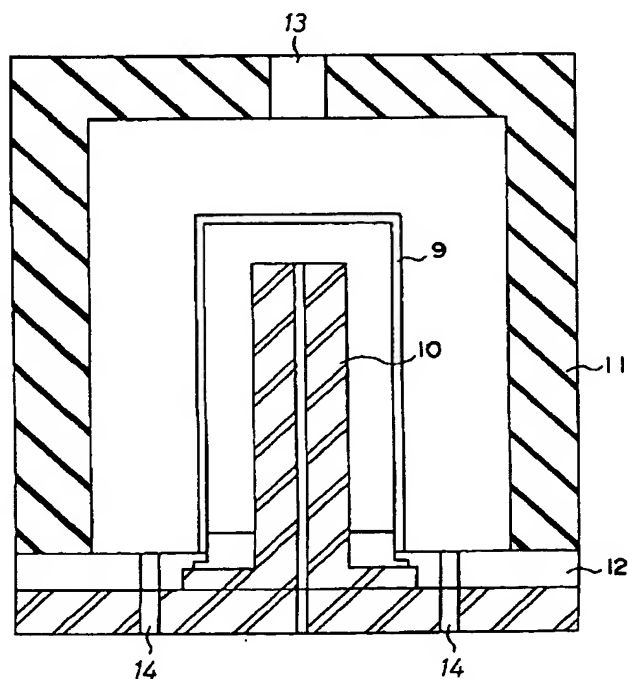
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(54) 【発明の名称】 プラスチックス材料からなる立体形状の容器に均一の膜厚の珪素酸化物被膜を形成する方法

(57) 【要約】

【目的】 プラスチックス材料からなる立体形状の容器に均一の膜厚の高ガス遮断性被膜を形成する方法を提供する。

【構成】 珪素酸化物薄膜の製膜温度よりT. g. が高いプラスチック材料からなる立体形状の容器の被膜を形成しない表面側に容器の被膜を形成する表面と電極表面との距離が10mm以下でほぼ一定である高周波電極を配置し、被膜を形成する表面側に容器の表面と電極表面との距離が高周波電極と被膜を形成する容器表面との距離より大きくほぼ一定であるアース電極を設置し、CVD法により生成した珪素酸化物のプラズマを容器とアース電極の間に導入して放電ガス圧0.0005~0.05torrで容器のアース電極と対向した表面に珪素酸化物薄膜を均一の膜厚に付着させることを特徴とするプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法である。



【特許請求の範囲】

【請求項 1】 珪素酸化物薄膜の製膜温度より T. g. が高いプラスチック材料からなる立体形状の容器の被膜を形成しない表面側に容器の被膜を形成する表面と電極表面との距離が 10 mm 以下でほぼ一定である高周波電極を配置し、被膜を形成する表面側に容器の表面と電極表面との距離が高周波電極と被膜を形成する容器表面との距離より大きくほぼ一定であるアース電極を設置し、CVD 法により生成した珪素酸化物のプラズマを容器とアース電極の間に導入して放電ガス圧 0.0005

【請求項 2】 容器表面とアース電極の距離が 11～100 mm でほぼ一定である、請求項 1 に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

【請求項 3】 アース電極が容器被覆面とほぼ同一形状の対向表面を有する 1 ケの電極である、請求項 1 または 2 に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

【請求項 4】 高周波電極が容器の被覆面とほぼ同一形状の内面を有する 1 ケの電極である、請求項 1 ないし 3 のいずれか 1 項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

【請求項 5】 プラスチック材料からなる立体形状の容器の表面に形成した珪素酸化物薄膜が屈折率 1.4～1.5 で膜厚が 300～2000 Å である、請求項 1 ないし 4 のいずれか 1 項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

【請求項 6】 珪素酸化物薄膜の製膜温度より T. g. が高いプラスチック材料からなる立体形状の容器の被膜を形成しない表面側に容器の被覆を形成する表面と電極表面との距離が 10 mm 以下でほぼ一定である高周波電極を配置し、被膜を形成する表面側に容器の表面と電極表面との距離が高周波電極と被膜を形成する容器表面との距離より大きくほぼ一定であるアース電極を設置し、低温プラズマ法により少なくとも珪素、酸素、炭素からなる有機シリコン化合物をプラズマとなし、該プラズマを容器とアース電極の間に導入して放電ガス圧 3×10^{-3} ～ 3×10^{-2} torr で重合して容器内面に珪素化合物重合体薄膜を形成し、ついで CVD 法により生成した珪素酸化物のプラズマを供給して放電ガス圧 0.0005～0.05 torr で珪素化合物薄膜上に珪素酸化物の被膜を形成することを特徴とするプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪

素酸化物薄膜を被覆する方法。

【請求項 7】 珪素化合物被膜が、屈折率 2.0～2.3 で膜厚が 0.005 μm～0.05 μm あり、珪素酸化物被膜が屈折率 1.4～1.5 で膜厚が 300～2000 Å である、請求項 6 に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は包装用等に使用されるプラスチック材料からなる容器にガス遮断性に優れた透明な珪素化合物の薄膜を被覆する方法に関する。

【0002】

【従来の技術】 包装材は内容物の保護と保存のためガスの透過を防ぐ必要があり、従来種々の試みがなされている。例えば、珪素酸化物やアルミニウム酸化物等の無機物の被覆層を設けたり、ポリ塩化ビニリデン等のガス遮断性樹脂層を積層したり、アルミ箔の金属フィルムを積層することが試みられて来た。この他特開平 3-183759 号公報にはプラスチックフィルムにそのプラスチックと同じ合成樹脂を真空蒸着や、スパッタリングによって薄膜状で被覆して有機物層を形成し、その上に無機物を蒸着して有機物と無機物の混合層を形成し、さらにその上に無機物層を形成した積層フィルムが示されている。このプラスチックは、被覆層の無機物とは全く異なる物質であって親和性が乏しいためプラスチックに同じ合成樹脂を薄膜状に被覆し、無機被覆の定着性を良くするために中間に合成樹脂と無機物のブレンド層を形成したものであるが、ブレンド層の表面は無機物のみの面ではなく合成樹脂の面も存在するので無機物層の定着性は期待した程には向上しない。また、合成樹脂と無機物を 2 工程で蒸着することはシート状物以外例えば成形体には適用出来ない。さらに合成樹脂は蒸着すると分子量が低下するのでこのプラスチック材料からなる容器は加工性が劣化する。本発明者は先に特開平 5-345383 号発明と特願平 5-224903 号発明を出願した。これ等の発明は従来の包装材とは全く異なる画期的な発明であり、従来の包装材の欠点は解決された。しかしながら、立体的構造を有する容器については均一の膜厚の被膜を形成することは出来るが、超精密な均一の膜厚の被膜を形成することにはやや不十分な点があった。そして特殊な用途、例えば特殊な薬品等の包装には超精密な膜厚が要求される。

【0003】

【発明が解決しようとする課題】 本発明は立体的構造の容器に、例えば膜厚の差が 200 Å 以下の超精密な膜厚の被膜を形成し、前述の膜厚不均一の問題を解決しガス遮断性を著るしく向上するものである。

【0004】

【課題を解決した手段】 本発明は、

「1. 珪素酸化物薄膜の製膜温度よりT. g. が高いプラスチック材料からなる立体形状の容器の被膜を形成しない表面側に容器の被覆を形成する表面と電極表面との距離が10mm以下でほぼ一定である高周波電極を配置し、被膜を形成する表面側に容器の表面と電極表面との距離が高周波電極と被膜を形成する容器表面との距離より大きくほぼ一定であるアース電極を設置し、CVD法により生成した珪素酸化物のプラズマを容器とアース電極の間に導入して放電ガス圧0.0005~0.05torrで容器のアース電極と対向した表面に珪素酸化物薄膜を均一の膜厚に付着させることを特徴とするプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

2. 容器表面とアース電極の距離が11~100mmでほぼ一定である、1項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

3. アース電極が容器被覆面とほぼ同一形状の対向表面を有する1ヶの電極である、1項または2項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

4. 高周波電極が容器の被覆面とほぼ同一形状の内面を有する1ヶの電極である、1項ないし3項のいずれか1項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

5. プラスチック材料からなる立体形状の容器の表面に形成した珪素酸化物薄膜が屈折率1.4~1.5で膜厚が300~2000Åである、1項ないし4項のいずれか1項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

6. 珪素酸化物薄膜の製膜温度よりT. g. が高いプラスチック材料からなる立体形状の容器の被膜を形成しない表面側に容器の被覆を形成する表面と電極表面との距離が10mm以下でほぼ一定である高周波電極を配置し、被膜を形成する表面側に容器の表面と電極表面との距離が高周波電極と被膜を形成する容器表面との距離より大きくほぼ一定であるアース電極を設置し、低温プラズマ法により少なくとも珪素、酸素、炭素からなる有機シリコン化合物をプラズマとなし、該プラズマを容器とアース電極の間に導入して放電ガス圧 3×10^{-3} ~ 3×10^{-2} torrで重合して容器内面に珪素化合物重合体薄膜を形成し、ついでCVD法により生成した珪素酸化物のプラズマを供給して放電ガス圧0.0005~0.05torrで珪素化合物薄膜上に珪素酸化物の被膜を形成することを特徴とするプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。

7. 珪素化合物被膜が、屈折率2.0~2.3で膜厚

が0.005μm~0.05μmあり、珪素酸化物被膜が屈折率1.4~1.5で膜厚が300~2000Åである、6項に記載されたプラスチック材料からなる立体形状の容器にガス遮断性に優れた珪素酸化物薄膜を被覆する方法。」に関する。

【0005】

【作用】本発明の特殊の作用を奏する第1の特徴は、立体形状の容器の外部に容器を包囲した外部電極を配置し、容器の外面と外部電極表面との距離がほぼ一定であり、また容器の内部には容器の内面と電極表面との距離がほぼ一定である内部電極を配置したことである。更に容器の内面に薄膜を被覆する場合は外部電極の表面と容器内面との距離が10mm以下であり、また容器の外面に薄膜を被覆する場合は内部電極の表面と容器外面との距離が10mm以下であることが特徴である。電極と容器表面の距離を一定に保つのは電界強度分布を一定とするためである。高周波電極と容器の被覆を設ける表面との距離は10mm以下でなければならない。10mm以上となると急激に被膜のガス遮断性が低下する問題が生ずるからである。またアース電極と容器の被覆表面との距離は被覆を設ける面と高周波電極との距離より大きくなければならない。容器の被覆を設ける表面と高周波電極の距離と、容器の被覆を設ける表面とアース電極の距離が等しいと安定した放電が得られない。そして本発明の放電条件では放電は電極と容器表面の距離の大きい方で放電する。それ故本発明では容器表面とアース電極の距離を大きくしてこの間で放電させて被膜を形成するのである。アース電極と容器表面の距離は好ましくは11~100mmであり、好ましくは11~70mmである。

【0006】本発明の第2の特徴は、一ヶのアース電極と一ヶの高周波電極を使用することである。このような両電極を併用することにより電界の強度分布は精密に一定となり形成される被膜の厚さは均一となる。

【0007】本発明の第3の特徴は、CVD法を用い珪素酸化物のプラズマを生成させて放電ガス圧が0.0005torr以下では製膜速度が極端に低下し、実質製膜できない状態であり、またガス圧が0.05torr以上では被膜のガス遮断性が急激に低下する問題が生ずる。

【0008】本発明の第4の特徴は被覆を行う容器として珪素酸化物薄膜の製膜温度よりT. g. が高いプラスチック材料で形成した容器を使用することである。超精密な薄膜を形成するためには製膜時には容器の変形を避けなければならないからである。このような第1の特徴~第4の特徴が組合されて、珪素酸化物のプラズマは電極表面と器壁の間に導入される。この間の電界強度分布が一定であるのでプラズマ濃度が一定となり珪素酸化物は均一な厚みで器壁上に析出し被覆される。こうして一定の厚みの珪素酸化物被膜が形成されるのである。

【0009】内部電極も外部電極も夫々1ヶでなければならず、電極を複数個使用することは避けなければならない。複数個の電極を用いると、CVD法を用いても均一な被膜を形成することができない。何故均一な被膜が形成されないのか本発明者は種々研究した。例えば図3に示すように複数の電極を容器の外面との距離が一定となるように配置し、CVD法により珪素酸化物を被覆したところ後の比較例で示すように被膜の厚さは一定にならなかった。さらに容器を一定の速度で回転させつつ被覆を行った場合、膜厚は均一になるが、被覆された膜のガス遮断性は向上しなかった。本発明者は複数本の電極を用いたため、夫々の電極の有する電界強度分布が互いに干渉して影響し、プラズマの濃度が変化するため膜厚が均一にならず、また容器を回転させた場合、異なる電界強度により形成された膜の混合体であることからガス遮断性に優れた膜が形成されないのと考えている。

【0010】本発明はCVD法を用いるが、高周波、交流そして直流を用いたCVD法等が使用される。本発明により形成される珪素酸化物被膜は屈折率が1.4～1.5で膜厚が300～2000Åである。膜厚が300Å以下では連続膜が得られず、ガス遮断性が向上せず、また2000Å以上被覆してもあまりガス遮断性の向上がみられず、逆に膜が内部応力によって破壊する問題が生ずる。本発明でCVD法で珪素酸化物プラズマを形成するために使用する材料は、SiH₄とNO_x、ガスや酸素ガスまたTEOS（テトラエトキシシラン）及びHMDSO（ヘキサメチルジシロキサン）等有機珪素化合物とNO_x、酸素ガス又プラズマ補助ガスとしてHeやArガスなども使用される。このようにして形成された珪素酸化物被膜は優れたガス遮断効果を奏し、通常の用途には非常に優れた容器である。

【0011】本発明の第5の特徴はアース電極を容器の内面側に配置するか外面側に配置するかを選択することによりどちらの面にも被覆することが出来る。またアース電極の位置を変えて複数回行うことにより内外両面を被覆することもできる。

【0012】本発明で珪素酸化物被膜を形成するに使用される珪素化合物は、シランやビニルエトキシシラン、フェニルトリメトキシシラン等の液状のモノマーである。

【0013】本発明はまた、珪素酸化物薄膜の製膜温度よりT_gの高いプラスチック材料からなる立体形状の容器の被膜を形成しない側に、容器の被覆を設ける表面と電極表面との距離が10mm以下でほぼ一定である高周波電極を設置し、また容器の被膜を形成する側には容器表面と電極表面の距離が高周波電極と容器表面の距離より大きくほぼ一定であるアース電極を配置して、低温プラズマ法により少くとも珪素、酸素、炭素からなる有機シリコン化合物をプラズマとなし、該プラズマを

容器表面とアース電極の間に供給し、ガス圧 $3 \times 10^{-3} \sim 3 \times 10^{-2}$ torrで重合して容器内面に珪素化合物重合体薄膜を形成し、ついでCVD法により生成した珪素酸化物のプラズマを供給して放電がガス圧0.0005～0.05 torrで珪素化合物薄膜上に珪素酸化物の被膜を形成することを特徴とするプラスチック材料からなる容器に均一の膜厚の珪素酸化物被膜を形成する方法も包含する。この二層からなる被膜はガス遮断性が優れるとともに水蒸気透過量が $0.1 \text{ g/m}^2 \text{ day}$ 以下の非常に高い水蒸気遮断効果を奏する。この珪素化合物重合体被膜と珪素酸化物被膜を、アース電極と高周波電極を配設して形成すると両被膜とも均一な被膜が形成されるので、ガス遮断性が著しく向上する。

【0014】何故この二種の層がこの順序で積層されるとこのような特別の効果が奏されるのかその学問的説明は必ずしも充分ではないが、本発明は反復再現する作用効果を奏する。本発明者は、珪素酸化物層のガス遮断効果は、被覆基体上に供給される珪素酸化物微粒子の安定定着性によるところが大きいと考える。即ち供給された粒子はプラスチック基体上を移動し最も安定な場所で安定化し定着する。この場合プラスチック基体の上に珪素、炭素、酸素を含む珪素化合物の重合体被膜が形成されていると珪素酸化物微粒子は良好に安定化し定着する。そしてその分布は均一となり、安定化した珪素酸化物粒子の上にさらに珪素酸化物微粒子が積み重なって珪素酸化物被覆が形成されるので緊密な被覆となるからであると考えている。

【0015】また第一層の珪素化合物重合体被膜と第二層の珪素酸化物被膜が夫々特定の屈折率の範囲内にあると $0.1 \text{ g/m}^2 \text{ day}$ 以下の超水蒸気ガス遮断性を示すことについてはより定着性の高い、欠陥の少ない緊密な被膜となるからであると考えている。

【0016】第1の有機珪素化合物重合体被覆層は第一層中の珪素、炭素、酸素の組成において、珪素15%以上、炭素20%以上そして残りが酸素を含有し、 $0.005 \mu\text{m} \sim 0.05 \mu\text{m}$ の薄い層である。被覆層の厚みがこれより厚くなるとガス遮断性が悪くなる。

【0017】このような第一層の特殊な有機珪素化合物重合体被覆は例えば、ヘキサメチルジシロキサン等の有機珪素化合物モノマーをプラズマ化し、プラスチック基体上で重合することによって形成することが出来る。この重合時のガス圧を 3×10^{-3} から 3×10^{-2} torrに調節することによって形成される被膜の屈折率を2.0～2.3にすることが出来る。従来、他の用途ではあるが知られているプラズマCVD法は放電ガス圧が0.数torrから数十torrの範囲であるから本発明で用いるプラズマCVD法が特殊であることがわかる。

【0018】本発明で使用する有機シリコン化合物モノマーとしてはビニルトリエトキシシラン、ビニルトリメ

トキシシラン、テトラメトキシシラン、テトラエトキシシラン、フェニルトリメトキシシラン、オクタメチルシクロテトラシロキサン、メチルトリメトキシシラン、メチルトリエトキシシラン、1133-テトラメチルジシロキサン、ヘキサメチルジシロキサン等である。これ等の化合物は珪素酸化物被膜の形成にも使用される。

【0019】

【実施例】本発明をわかり易いように実施例をあげて説明する。

【0020】実施例1

図1は本発明で使用した有機シリコン化合物被膜を形成する高周波プラズマCVD装置である。この装置はシランや常温液体モノマーを気体状態で導入する導入口6及び酸素ガス導入口7を備えた直径60cmのステンレス製ベルジャー型真空チャンパー1と日本電子株式会社製、高周波電源5、(13.56MHz、1.5KW、JEH-01B)及びマッチングボックス4そして直径13cmの円盤状高周波電極3、直径20cm、高さ1.5cmの円筒状アース電極2、両電極間に設置した試料用治具8等からなっている。この図1の装置は、有機珪素化合物被覆とガス遮断層であるシリコン酸化物膜の被覆の両方を行なうことが出来る。真空ポンプは油回転ポンプと油拡散ポンプを使用し、前処理及び成膜中は常にポンプを引き続け、前処理及び薄膜被覆試験を行なった。常温液体モノマーとしてはヘキサメチルジシロキサン(以下HMDSOと記す)、反応ガスとしては、酸素ガスを使用した。これらのガスはそれぞれ別ルートでチャンパー内に導入され、アース電極内で混合されチャンパー内に放出される。アース電極と高周波電極は平行(距離70mm)に配置し、試料として100 μ のポリカーボネート(以下PCと記す)シートを絶縁性試料治具によって、高周波電極とアース電極(高周波電極より5mm)に設置した。油回転ポンプと油拡散ポンプによりチャンパー内真空度を $2\sim 3\times 10^{-5}$ torr(電離真空計)まで真空に引き、チャンパー内真空度が 1×10^{-3} torrになるまで酸素ガスを導入し、続いてチャンパー内真空度が 2×10^{-3} torrになるまでHMDSO蒸気を導入した。高周波電源より入射電力200Wをマッチングボックスを経由し、チャンパー内に導入し、酸素とHMDSOの混合プラズマを発生させ、10分間保持し、PC試料上に酸化珪素物膜を形成した。この積層体の水蒸気透過量をMoccon社製水蒸気透過量測定器で測定し、表1に示した。

【0021】実施例2及び比較例1

高周波電極及びアース電極間に設置する試料の位置を高周波基板上、3、7、9、23、そして40mmに設置したこと以外は実施例1と同じ条件で、PC試料上に酸化珪素物膜を形成し、水蒸気透過量を測定し、表1に実施例1と共に示した。

【0022】

【表1】

| | 高周波電極-基板 間距離(mm) | 水蒸気透過量 $g/m^2\text{ day}$ |
|------|---------------------|------------------------------|
| 実施例1 | 5 | 0.07 |
| 実施例2 | 0 | 0.10 |
| | 3 | 0.09 |
| | 7 | 0.07 |
| | 9 | 0.10 |
| 比較例1 | 23 | 1.3 |
| | 40 | 3.1 |

【0023】実施例3及び比較例2

試料に厚みが100 $\mu\sim 280\mu$ でガラス転移温度(以下 T_g と記す)が -15°C から 105°C のプラスチックシートを使用した以外は実施例1と同じ条件で、試料上に酸化珪素物膜を形成し、水蒸気透過量を測定し、表2に示した。光ファイバー式温度計により試料表面の温度を測定した結果、この条件では 45°C であった。

【0024】

【表2】

| | 基板の $T_g(^\circ\text{C})$ | 水蒸気透過量 |
|------|---------------------------|--------|
| 実施例3 | 125 | 0.03 |
| | 115 | 0.04 |
| | 105 | 0.03 |
| | 97 | 0.04 |
| | 91 | 0.08 |
| | 67 | 0.1 |
| 比較例2 | -10 | 0.4 |

【0025】実施例4

図2は本発明に用いる容器外面被覆用電極の断面を示す説明図である。図中の9はポリエチレンテレフタレート(以下PET)製有底円筒形状容器である。10は内部高周波電極であって、その外表面は有底円筒形状容器の外表面と同様な形状となっている。そして電極10の外表面と容器外表面の距離は約5mmで一定となっている。11は外部アース電極で、電極11の内面は有底円筒形状容器9の外表面とほぼ同じ形状であって、両者の距離は約12mmでほぼ一定である。アース電極11と高周波電極10は絶縁体12を介して配置されており、アース電極11の上部にはガス導入口13が又容器外面被覆用電極の下部にはガス排気口14が設置されている。反応ガス及びモノマーガスはガス導入口13より電極内に導入され、プラズマ化され、有底円筒形状容器9の外表面に沿って流れ、ガス排気口14より電極外に排気される。この電極では珪素酸化物被膜は有底円筒形状容器9の外表面に形成される。有底円筒形状容器9を配置した容器外面被覆用電極により、図1に示す装置を使用して、容器

外表面に珪素酸化物被膜を形成した。酸化珪素物被膜の形成は、図 1 中の試料用治具 8 を取り外し、図 2 の容器外面被覆用電極を図 1 中の高周波電極 3 アース電極 2 間に配置し、円筒状アース電極 2 と容器外面被覆用電極のアース電極 1 1 を接続し、又円盤状高周波電極 3 と容器外面被覆用高周波電極 1 0 を接続した。油回転ポンプと油拡散ポンプによりチャンバー内真空度を $2 \sim 3 \times 10^{-5}$ torr (電離真空計) まで真空に引き、チャンバー内真空度が 1×10^{-3} torr になるまで酸素ガスを導入し、続いてチャンバー内真空度が 2×10^{-3} torr になるまで HMDSO 蒸気を導入した。高周波電源より入射電力 200W をマッチングボックスを経由し、チャンバー内に導入し、酸素と HMDSO の混合プラズマを発生させ、10 分間保持し、有底円筒形状容器の外表面に酸化珪素物膜を形成した。有底円筒形状容器の胴部の酸化珪素物膜厚分布と水蒸気透過量を測定し、表 3 に示した。

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* 【0026】比較例 3

図 3 に示すように、実施例 4 と同じ有底円筒形状容器 9 の外側に円筒形状容器外面から等距離に 4 本の外部高周波電極 1 5 を円筒中心より 90 度の等角度となる位置に配置した以外は実施例 4 と同じ条件として被覆を行った。その有底円筒形状容器 9 の胴部の酸化珪素物膜厚分布と水蒸気透過量を測定し、実施例 4 と共に表 3 に示した。図 4 は図 3 の被覆装置を上方からみた説明図であって、測定位置 0D、45D、90D が明示されている。

【0027】比較例 4

有底円筒形状容器 1 を 4 rpm で軸回転させること以外は比較例 3 と同じ条件として被覆を行った。その有底円筒形状容器の胴部の酸化珪素物膜厚分布と水蒸気透過量を測定し、実施例 4、比較例 3 と共に表 3 に示した。

【0028】

【表 3】

*

| 測定位置 | 膜厚 (Å) | | | 屈折率 | | | 水蒸気透過量 g/m ² day |
|-------|--------|------|-----|------|------|------|--------------------------------|
| | 0D | 45D | 90D | 0D | 45D | 90D | |
| 実施例 4 | 950 | 980 | 930 | 1.45 | 1.47 | 1.44 | 0.02 |
| 比較例 3 | 510 | 1680 | 620 | 1.42 | 1.69 | 1.44 | 1.85 |
| 比較例 4 | 940 | 990 | 950 | 1.55 | 1.60 | 1.56 | 1.05 |

【0029】実施例 5

図 5 は本発明に用いる容器内面被覆用電極の断面を示す説明図である。図中の 9 は環状オレフィンコポリマー (以下 C O C) 製のカップ形状容器である。1 5 は外部高周波電極であって、その内表面はカップ形状容器の内面と同様な形状となっている。そして電極 1 5 の内表面と容器内表面の距離は約 5 mm で一定となっている。1 6 は内部アース電極で、電極 1 6 の外面はカップ形状容器 9 の内面とほぼ同じ形状であって、両者の距離は約 20 mm でほぼ一定である。アース電極 1 6 と高周波電極 1 5 は絶縁体 1 2 を介して配置されており、アース電極 1 6 の下部にはガス導入口 1 3 が又アース電極の上部にはガス排気口 1 4 が設置されている。反応ガス及びモノマーガスはガス導入口 1 3 より電極内に導入され、プラズマ化され、カップ形状容器 1 の内面に沿って流れ、ガス排気口 1 4 より電極外に排気される。この電極では珪素酸化物被膜はカップ形状容器 9 の内表面に形成される。カップ形状電極を配置した容器内面被覆用電極により、図 1 に示す装置を使用して、容器内表面に珪素酸化物被膜を形成した。酸化珪素物被膜の形成は、図中の試料用治具 8 を取り外し、図 5 の容器内面被覆用電極を図 1 中の高周波電極 3 とアース電極 2 間に配置し、円筒状アース電極 2 と容器内面被覆用電極のアース電極 1 6 を接続し、又円盤状高周波電極 3 と容器内面被覆用高周波電極 1 5 を接続し、SiH₄ ガスをモノマー導入口から導入し、酸素を酸素ガス導入口から導入して、これらの混合ガスプラズマを形成し、放電圧力を 3×10^{-3} t

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40

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orr でカップ剛状容器の内面に酸化珪素膜を析出させて行った。酸化珪素膜を被覆したカップ上容器の水蒸気透過量を測定した結果、0.02 g/m² day (40℃90%RH) であった。

【0030】実施例 6

ポリエチレンナフタレート (以下 PEN と記す) 製有底円筒形状容器を使用し、容器外面被覆用電極により、図 2 に示す装置を使用して、容器外表面に HMDSO 重合体被膜と珪素酸化物被膜を形成した。被膜方法は有底円筒形状容器と以下に記す条件以外は実施例 4 と同じ条件として被覆を行った。油回転ポンプと油拡散ポンプによりチャンバー内真空度を $2 \sim 3 \times 10^{-5}$ torr (電離真空計) まで真空に引き、チャンバー内真空度が 3×10^{-3} torr $\sim 10 \times 10^{-3}$ torr になるまで HMDSO 蒸気を導入した。高周波電源より入射電力 400W をチャンバーに導入し、HMDSO のプラズマを発生させ、1 分間保持し、有底円筒形状容器の外表面に HMDSO 重合体被膜を形成した。続いて油回転ポンプと油拡散ポンプによりチャンバー内真空度を $2 \sim 3 \times 10^{-5}$ torr まで真空に引き、実施例 5 と同様に、HMDSO 重合膜の上に珪素酸化物の被膜を形成した。これら被膜を被覆した有底円筒形状容器の膜の屈折率、膜厚をエリプソメーターで、そして重量法により、水蒸気透過量を測定し、表 4 に示した。

【0031】

【表 4】

| | H M D S O | | H M D S O 膜 | | 二層膜の水蒸気透過量 |
|-------|-----------|-------|-------------|-----|------------|
| | 濃 度 | 被覆時間 | 屈折率 | 膜厚 | |
| 実施例 6 | 3 | 0.5 分 | 2.05 | 60 | 0.04 |
| | 3 | 1.0 分 | 2.05 | 100 | 0.03 |
| | 3 | 2.0 分 | 2.05 | 210 | 0.05 |
| | 8 | 0.5 分 | 2.25 | 80 | 0.02 |
| | 8 | 1.0 分 | 2.25 | 150 | 0.02 |
| | 8 | 2.0 分 | 2.25 | 320 | 0.03 |
| | 10 | 0.5 分 | 2.04 | 120 | 0.05 |
| | 10 | 1.0 分 | 2.04 | 240 | 0.08 |
| | 10 | 2.0 分 | 2.04 | 480 | 0.08 |

【0032】(註) H M D S O 濃度の単位： $\times 10^{-3}$ torr、

膜厚の単位；オングストローム、

水蒸気透過量の単位； $\text{g}/\text{m}^2 \text{ day}$ 、at 40°C 90% RH、

【0033】比較例 5

H M D S O の濃度が 1.5×10^{-3} torr 及び 2.0

$\times 10^{-3}$ torr として H M D S O 膜の被覆時間が *20

*0.2 及び 5 分であること以外は実施例 6 に同じ有底円筒形状 P E N 容器の外面に被覆した H M D S O 膜の屈折率及び膜厚をエリプソメーターで測定し、又 H M D S O 膜と珪素酸化積層膜の水蒸気透過量を重量法で測定し、表 5 にした。

【0034】

【表 5】

| | H M D S O | | H M D S O 膜 | | 二層膜の水蒸気透過量 |
|-------|-----------|-------|-------------|------|------------|
| | 濃 度 | 被覆時間 | 屈折率 | 膜厚 | |
| 比較例 5 | 2 | 0.2 分 | 1.76 | 30 | 0.15 |
| | 2 | 5 分 | 1.78 | 770 | 0.45 |
| | 20 | 0.5 分 | 1.68 | 300 | 0.32 |
| | 20 | 5 分 | 1.66 | 6000 | 0.47 |
| 未 被 覆 | | | | | 0.49 |

【0035】(註) H M D S O の濃度の単位： $\times 10^{-3}$ torr、

H M D S O 膜の膜厚；オングストローム、

二層膜の水蒸気透過量の単位； $\text{g}/\text{m}^2 \text{ day}$ 、at 40°C 90% RH、

【0036】実施例 7

ポリエチレンナフタレート（以下 P E N と記す）製有底円筒形状容器を使用し、容器外面被覆用電極により、図 2 に示す装置を使用して、容器外表面に H M D S O 重合体被膜と珪素酸化物被膜を形成した。被膜方法は有底円筒形状容器と以下に記す条件以外は実施例 4 と同じ条件として被覆を行った。油回転ポンプと油拡散ポンプによりチャンパー内真空度を $2 \sim 3 \times 10^{-5}$ torr（電離真空計）まで真空に引き、チャンパー内真空度が 4×10^{-3} torr になるまで H M D S O 蒸気を導入し

た。高周波電源より入射電力 400W をチャンパー内に導入し、H M D S O のプラズマを発生させ、1 分間保持し、有底円筒形状容器の外面に H M D S O 重合体被膜を形成した。続いて油回転ポンプと油拡散ポンプによりチャンパー内真空度を $2 \sim 3 \times 10^{-5}$ torr まで真空に引き、H M D S O 蒸気と酸素の濃度比（電離真空計によるチャンパー内真空度の比率；H M D S O / 酸素）を 0.5 ～ 2.5 の範囲で、かつ酸化珪素膜の被覆時間を 5 ～ 20 分以外は実施例 5 と同様にして、H M D S O 重合膜の上に珪素酸化物の被膜を形成した。これら被膜を被覆した有底円筒形状容器の膜の屈折率、膜厚をエリプソメーターで、そして重量法により、水蒸気透過量を測定し、表 6 に示した。

【0037】

【表 6】

| | HMDSO/O ₂ の比率 | 酸化珪素膜 の被覆時間 | 酸化珪素膜 | | 二層膜の 水蒸気透過量 |
|-------|-----------------------------|----------------|-------|------|----------------|
| | | | 屈折率 | 膜厚 | |
| 実施例 7 | 0.5 | 5.0 | 1.43 | 510 | 0.03 |
| | 0.5 | 10.0 | 1.44 | 1060 | 0.02 |
| | 0.5 | 20.0 | 1.44 | 1980 | 0.02 |
| | 1.0 | 5.0 | 1.45 | 490 | 0.02 |
| | 1.0 | 10.0 | 1.45 | 1080 | 0.02 |
| | 1.0 | 20.0 | 1.46 | 2010 | 0.02 |
| | 2.5 | 5.0 | 1.46 | 520 | 0.03 |
| | 2.5 | 10.0 | 1.46 | 1050 | 0.04 |
| | 2.5 | 20.0 | 1.46 | 2030 | 0.05 |

【0038】(註) 酸化珪素膜の被覆時間の単位；
分、

酸化珪素膜の膜厚の単位；オングストローム、
二層膜の水蒸気透過量の単位； $\text{g}/\text{m}^2 \text{ day}$ 、at
40°C 90% RH、

【0039】比較例 6

HMDSO 蒸気と酸素の濃度比（電離真空計によるチャ
ンバー内真空度の比率；HMDSO/酸素）を 0.5 と *20

* 5 で、かつ酸化珪素膜の被覆時間を 2 分及び 2.5 分以外
は実施例 7 と同様にして、HMDSO 重合膜の上に珪素
酸化物の被膜を形成した。これら被膜を被覆した有底円
筒形状容器の膜の屈折率、膜厚をエリプソメーターで、
そして重量法により、水蒸気透過量を測定し、表 7 に示
した。

【0040】

【表 7】

| | HMDSO/O ₂ の比率 | 酸化珪素膜 の被覆時間 | 酸化珪素膜 | | 二層膜の 水蒸気透過量 |
|-------|-----------------------------|----------------|-------|------|----------------|
| | | | 屈折率 | 膜厚 | |
| 比較例 6 | 0.2 | 2 分 | 1.38 | 180 | 0.46 |
| | 0.2 | 25 分 | 1.39 | 2350 | 0.14 |
| | 5.0 | 2 分 | 1.59 | 190 | 0.48 |
| | 5.0 | 25 分 | 1.60 | 2530 | 0.25 |
| 未被覆 | | | | | 0.49 |

【0041】(註) 酸化珪素膜の膜厚の単位；オング
ストローム、

二層膜の水蒸気透過量の単位； $\text{g}/\text{m}^2 \text{ day}$ 、at
40°C 90% RH、

【0042】

【発明の効果】本発明は立体形状のプラスチック容器
に均一の膜厚で一定範囲の屈折率の珪素酸化物薄膜を形
成するので、ガスバリア性の優れた容器を提供すること
が出来る。

【図面の簡単な説明】

【図 1】本発明で使用する高周波プラズマ CVD 装置の
説明図である。

【図 2】本発明で使用する容器外面被覆装置の説明図で
ある。

【図 3】比較例の説明図である。

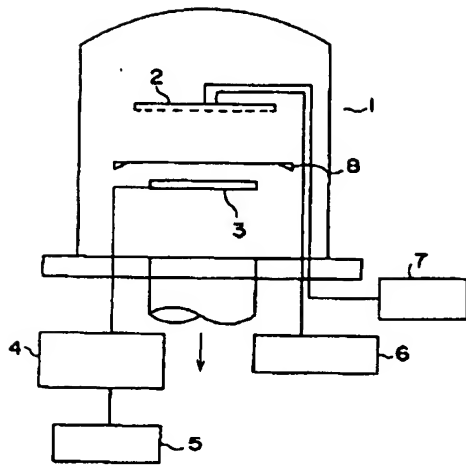
【図 4】図 3 の装置の測定位置を示す説明図である。

【図 5】本発明で使用する容器内面被覆装置の説明図
である。

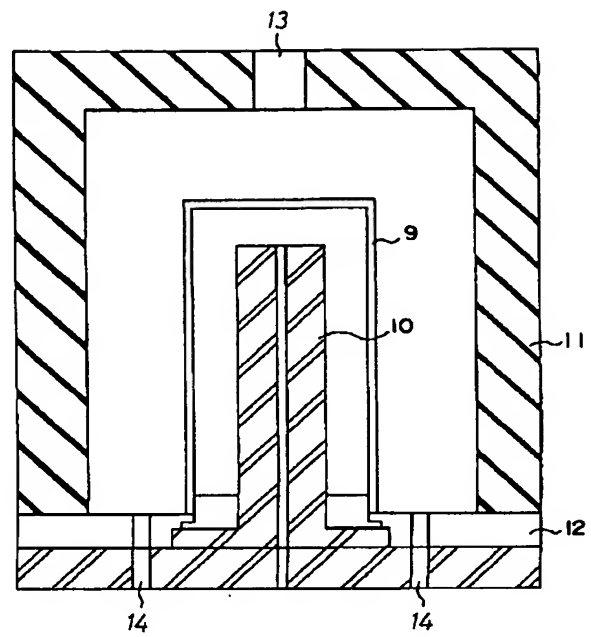
【符号の説明】

- 1 真空チャンバー
- 2 アース電極
- 3 高周波電極
- 4 マッチボックス
- 5 高周電源
- 6 ガス導入口
- 7 ガス入口
- 8 真空チャンバー試料用治具
- 9 円筒状容器
- 10 内部高周波電極
- 11 外部アース電極
- 12 絶縁体
- 13 ガス導入口
- 14 ガス排出口
- 15 外部高周波電極
- 16 内部アース電極

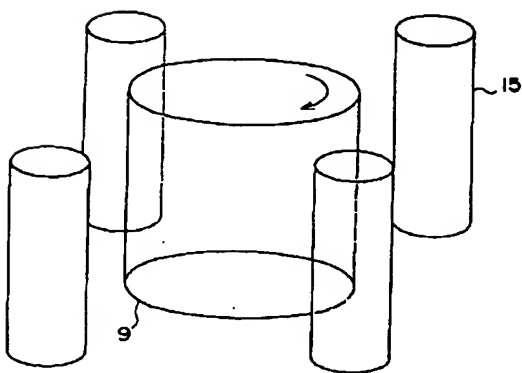
【図 1】



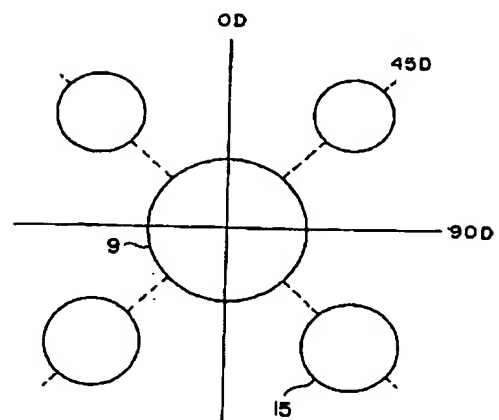
【図 2】



【図 3】



【図 4】



A cross-sectional view of a semiconductor device. The device features a central vertical structure (13) surrounded by a frame (9). The frame is composed of multiple layers, including a top layer (12) and a bottom layer (15). The central structure is flanked by two vertical regions (14 and 15) and a central region (16). The entire structure is embedded within a substrate (10).

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技術表示箇所